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PREPARATION OF TRIAZATRIPHENYLENE CATIONS, PROMISING CHEMOSENSORS FOR NITRO COMPOUNDS

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Triphenylene and its poly(hetero)aromatic derivatives are of significant interest as potential chemical sensors for polynitroaromatic compounds due to their photoluminescent properties and their ability to form stable, non-fluorescent π-complexes with electron deficient substrates [1, 2]. In such an interaction the efficiency of photoluminescence quenching depends on the rate of electron transfer from the polyaromatic compound as donor to the nitro compound as acceptor. According to literature data, the efficiency of this electronic interaction can be increased by the introduction of Lewis acid fragments, e.g., metals or azinium cations into the poly(hetero)aromatic sensor molecule [3]. The structure of the polynitro compounds include Lewis base fragments (the oxygen atoms of the nitro groups), and hence an interaction with cations and other Lewis acids accelerates the "donor-acceptor" electronic communication, thus enhancing the photoluminescence quenching [4].

The most frequently used method for preparing azatriphenylenes is the Skraup synthesis [5, 6], which requires forcing conditions. Contemporary synthetic methods frequently use hard to obtain alkenes or arylacetylenes in transition metal-catalyzed cycloaddition reactions with aromatic substrates [7, 8]. On the other hand, a method of synthesizing aliphatic triphenylene precursors by cyclotrimerization of cyclohexanone [9] is widely known, and we have previously reported the preparation of 2-R-5,6,7,8,9,10,11,12-octahydro[1,2,4]triazino[1,6-*f*]phenanthridin-13-ium-4-olates by reaction of 3-R-1,2,4-triazin-5(4*H*)-ones with cyclohexanone under acid catalysis conditions [10]. The 1,2,4-triazines **1a**,**b** prepared in this way are of interest as triazatriphenylene precursors.

We have used several methods for the aromatization of compounds **1a**,**b** to the corresponding triphenylenes. The most effective was refluxing of compounds **1a**,**b** in *o*-xylene solution for 24 h in the presence of 2,3-dichloro-5,6-dicyanobenzoquinone (6 equivalents). The reaction products were obtained in up to 60% yield. The structure of the compounds obtained was confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass

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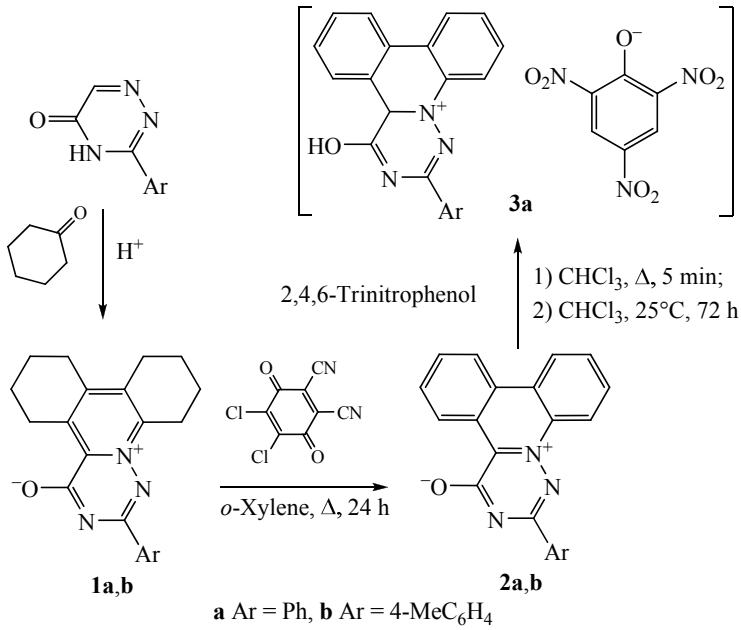
spectrometry, and elemental analysis. The ^{1}H NMR spectra unambiguously showed an azatriphenylene type aromatic structure, as evidenced by the presence of multiplets corresponding to the protons of phenylene fragments and aromatic substituents in the region of 7.87-10.64 ppm.

In contrast to the aliphatic precursors, the obtained products exhibited intense photoluminescence (λ_{max} 429-430 nm). Fluorescence titration of compound **2a**,**b** solutions with dichloromethane solutions of 2,4-dinitrotoluene and 2,4,6-trinitrophenol (picric acid) showed strong fluorescence quenching with values of the Stern-Volmer quenching constant of K_{sv} ~10^3-10^4 M^{-1} [4]. Cocrystallization of the triazatriphenylene **2a** with 2,4,6-trinitrophenol in chloroform solution led to formation of the picrate **3a**, the elemental analysis of which indicated a 1:1 stoichiometry.



Therefore, we have prepared novel triazatriphenylene cations showing a great promise for the visual assay of nitroaromatic compounds.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 instrument (400 and 100 MHz, respectively) using $CDCl_3$ with TMS as internal standard. Mass spectra (electrospray ionization) were recorded on a Bruker Daltonics micrOTOF-Q II mass spectrometer. Elemental analysis was carried out on a Perkin-Elmer PE 2400 series II CHN analyzer. TLC analysis was performed on Merck 60F254 silica gel plates and visualized using UV light. Column chromatography was performed on neutral aluminum oxide (Acros Organics, Brockmann I, 50-200 μm, 60 Å). UV absorption spectra were recorded on a Perkin-Elmer Lambda 45 spectrophotometer. Luminescence spectra were recorded for solutions on a Cary Eclipse (Varian) spectrofluorimeter.

2-Aryl-5,6,7,8,9,10,11,12-octahydro[1,2,4]triazino[1,6-*f*]phenanthridin-13-ium-4-olates 1a,b were prepared by a previously reported method [10].

Preparation of Compounds 2a,b (General Method). The corresponding octahydrotriazatriphenylene **1** (0.4 mmol) was dissolved in *o*-xylene (60 ml), the oxidant 2,3-dichloro-5,6-dicyanobenzoquinone (0.18 g, 0.8 mmol) was added, and the mixture was refluxed for 7 h. An additional portion of the oxidant (0.18 g, 0.8 mmol) was added and the mixture was refluxed for another 7 h. A further aliquot of oxidant (0.18 g, 0.8 mmol) was added, and the mixture was refluxed for 10 h. The reaction mixture was then cooled to room temperature and filtered from the precipitate formed. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatograpy (eluent EtOAc). An analytically pure sample was prepared by recrystallization from MeCN.

2-Phenyl[1,2,4]triazino[1,6-*f*]phenanthridin-13-ium-4-olate (2a). Yield 78 mg (60%). Colorless crystals; mp >250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.55 (3H, m, H Ph); 7.87-8.05 (4H, m, H Ph, H Ar); 8.58 (2H, m, H Ar); 8.66 (1H, d, ^3J = 8.0, H Ar); 8.71 (1H, m, H Ar); 9.46 (1H, m, H-12); 10.61 (1H, d, ^3J = 8.0, H-5). ^{13}C NMR spectrum, δ, ppm: 121.3; 121.5; 122.9; 123.4; 126.5; 128.4; 128.5; 129.8; 130.4; 130.7; 131.2; 131.3; 131.6; 133.3; 134.8; 135.2; 146.3; 162.6; 166.0. UV spectrum (CH_2Cl_2), λ_{max}, nm: 260, 384, 405. Fluorescence spectrum (CH_2Cl_2, at λ_{ext} 405 nm), λ_{max}, nm: 429. Mass spectrum, *m*/*z* (I_{rel}, %): 324.11 $[M+H]^+$ (100). Found, %: C 77.78; H 3.89; N 12.85. $C_{21}H_{13}N_3O$. Calculated, %: C 78.00; H 4.05; N 12.99.

2-(*p*-Tolyl)[1,2,4]triazino[1,6-*f*]phenanthridin-13-ium-4-olate (2b). Yield 78 mg (58%). Colorless crystals; mp >250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.47 (3H, s, CH_3); 7.38 (2H, m, H Tol); 7.88-8.07 (4H, m, H Ar); 8.49 (2H, m, H Tol); 8.69 (1H, m, H Ar); 8.74 (1H, m, H Ar); 9.51 (1H, m, H-12); 10.64 (1H, d, ^3J = 8.8, H-5). Mass spectrum, *m*/*z* (I_{rel}, %): 338.13 $[M+H]^+$ (100). Found, %: C 78.13; H 4.32; N 12.23. $C_{22}H_{15}N_3O$. Calculated, %: C 78.32; H 4.48; N 12.45.

4-Hydroxy-2-phenyl[1,2,4]triazino[1,6-*f*]phenanthridin-13-ium Picrate (3a). A solution of compound **2a** (39 mg, 0.12 mmol) and 2,4,6-trinitrophenol (27 mg, 0.12 mmol) in chloroform (5 ml) was heated under reflux for 5 min, and the mixture obtained was left at room temperature for 72 h. The light-yellow precipitate was filtered off and dried in air. Yield 12 mg (18%). Yellow crystals; mp >250°C. Found, %:C 58.71; H 3.12. $C_{27}H_{16}N_6O_8$. Calculated, %: C 58.70; H 2.92.

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